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Predicting Heats of Formation of Energetic Materials Using Quantum Mechanical Calculations

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Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5066

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Betsy M. Rice, Sharmila V. Pai, and Jennifer Hare
Weapons and Materials Research Directorate, ARL

Abstract

Quantum mechanical calculations are used to predict gas, liquid, and solid heats of formation of energetic molecules. A simple atom-equivalent method converts quantum mechanical energies of molecules and their atomic constituents to gas-phase heats of formation of energetic materials. Functional relationships between heats of vaporization and sublimation and properties associated with quantum, mechanically determined electrostatic potentials of isolated molecules are established. These are used with the gas-phase heats of formation to predict condensed-phase heats of formation. The calculated gas-phase heats of formation have a root mean square (rms) deviation of 3.1 kcal/mol and a maximum deviation of 7.3 kcal/mol from 35 experimental values. The rms and maximum deviation of predicted heats of vaporization from 27 experimental values are 1.7 and 6.1 kcal/mol, respectively. The rms and maximum deviations of predicted heats of sublimation from 36 experimental values are 3.6 and 12.4 kcal/mol, respectively. The rms and maximum deviations of predictions of liquid heats of formation from 41 measured values (corresponding to 24 molecules) are 3.3 and 9.3 kcal/mol, respectively. Similarly, the rms and maximum deviations of predictions of solid heats of formation from 75 measured values (corresponding to 44 molecules) are 9.0 and 35.4 kcal/mol, respectively.

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BETSY M. RICE,* SHARMILA V. PAI, and JENNIFER HARE

U. S. Army Research Laboratory, Aberdeen Proving Ground, MD

Quantum mechanical calculations are used to predict gas, liquid, and solid heats of formation of energetic molecules. A simple atom-equivalent method converts quantum mechanical energies of molecules and their atomic constituents to gas-phase heats of formation of energetic materials. Functional relationships between heats of vaporization and sublimation and properties associated with quantum mechanically determined electrostatic potentials of isolated molecules are established. These are used with the gas-phase heats of formation to predict condensed-phase heats of formation. The calculated gas-phase heats of formation have a root mean square (rms) deviation of 3.1 kcal/mol and a maximum deviation of 7.3 kcal/mol from 35 experimental values. The rms and maximum deviations of predicted heats of vaporization from 27 experimental values are 1.7 and 6.1 kcal/mol, respectively. The rms and maximum deviations of predicted heats of sublimation from 36 experimental values are 3.6 and 12.4 kcal/mol, respectively. The rms and maximum deviations of predictions of liquid heats of formation from 41 measured values (corresponding to 24 molecules) are 3.3 and 9.3 kcal/mol, respectively. Similarly, the rms and maximum deviations of predictions of solid heats of formation from 75 measured values (corresponding to 44 molecules) are 9.0 and 35.4 kcal/mol, respectively. © 1999 by The Combustion Institute

INTRODUCTION

The availability of propellants with significantly improved impetus and controlled burning rate properties is essential to the successful development and deployment of new high-performance tank, artillery, electrothermal–chemical, and Naval bombardment systems. Design concepts for the formulation of these advanced propellants is a crucial emerging technology in the United States Department of Defense, where limited funds dictate optimization of time and resources. In previous times, formulators would develop propellant mixes in a series of trial-and-error formulations, and heats of formation of the ingredients (if unknown) were measured for use in calculations to predict the impetus of the propellant under gun firing conditions. The determination of impetus is one of the first steps in the screening process of propellant formulation. Candidate propellants that show enhanced performance receive additional study; poor performers are eliminated from further consideration. Waste emanating from measurement of heats of formation of unsuitable candidates can be reduced through development and use of

theoretical capabilities for prediction of this property. The research presented here describes such a development of theoretical capabilities to aid in the screening process of propellant formulation. In this work, we present computational tools that convert quantum mechanical calculations of energetic materials to heats of formation in the gas, liquid, and solid phases.

There are a variety of methods to predict gas-phase heats of formation from quantum mechanical information. One method uses known heats of formation of isolated atoms and calculated atomization energies (D_0) to predict gas-phase heats of formation of molecules [1].

$$\Delta_f H^0(A_x B_y, 0K) = x \Delta_f H^0(A, 0K)$$
$$+ y \Delta_f H^0(B, 0K) - \sum D_0$$

$$(1)$$

This method was found to reasonably predict the heats of formation for a variety of organic and inorganic molecules with the best predictions corresponding to those using the G2 level of theory [2, 3]. While the degree of accuracy of the predictions using this level of theory has been impressive, the calculations require computationally expensive electron correlation treatments which might be prohibitive for systems containing a large number of atoms or

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*Corresponding author: Dr. B. M. Rice, U.S. Research Laboratory, AMSRL-WM-BD, Aberdeen Proving Ground, MD 21005-5066. E-mail: betsyr@arl.mil

where computational resources are limited. The study also assessed the performance of the more computationally tractable density functional theory (DFT) [4–7] in calculating heats of formation [1, 8]. The DFT predictions (using the B3LYP density functional) [9], while not as good as the G2 predictions, are reasonable. A similar procedure for predicting heats of formation using a modest level of quantum mechanical theory has been shown to be accurate to a few kcal/mol [10]. The method, known as BAC-MP4, corrects for errors in the level of theory through empirical bond-additivity corrections. Melius applied this method to 90 molecular species, and reports an average deviation from experiment of 1.3 kcal/mol [10].

Another method of predicting gas-phase heats of formation is based on Hess' Law [11] and uses a combination of quantum mechanical and experimental information. Hess' Law states that the standard reaction enthalpy is expressed as:

$$\Delta H^{\circ}_{\text{Reaction}} = \Delta H^{\circ}_f \text{(Products)}$$
$$- \Delta H^{\circ}_f \text{(Reactants)} \qquad (2)$$

The standard heat of formation of a single component of a reaction (either product or reactant) can be determined using the reaction enthalpy, which can be obtained from quantum mechanical calculations, and reliable values of heats of formation of the remaining products and reactants. The accuracy of the prediction using Eq. 2 is increased if the reaction is isodesmic [12]. Isodesmic reactions, in which numbers of electron pairs and chemical bond types are conserved in the reaction, allow for a cancellation of errors inherent in the approximate treatment of electron correlation in the solutions to the quantum mechanical equations. To illustrate, we predicted gas-phase heats of formation of 1,3,5-trinitro-1,3,5-s-triazine (RDX) (experimental value = 45.8 kcal/mol [13]) using Eq. 2. We calculated the heat of reaction of

$$3CH_2NNO_2 \rightarrow RDX$$
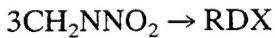
using DFT at the B3LYP/6-31G* level [9, 10, 14] and combined this with a reported heat of formation of the reactant, CH_2NNO_2 (33.6 kcal/mol) [15]. The predicted heat of formation for RDX is 52.8 kcal/mol, ~7 kcal/mol greater than the experimental value. This method of calculation, while giving a reasonable prediction, requires reliable values of heats of formation of other components of the reaction.

Atom equivalent schemes are used to convert quantum mechanical energies of formation of atoms to heats of formation for various classes of molecules. The gas-phase heat of formation using atom equivalents is represented as:

$$\Delta H_i = E_i - \sum n_j \epsilon_j \qquad (3)$$

where E_i is the energy of molecule i, ϵ_j (denoted as an "atom equivalent") is defined as $\epsilon_j = (E_j - x_j)$, E_j is the energy of an atom j that is a component of molecule i, n_j is the number of j atoms in molecule i, and x_j is the correction for atom j at the level of theory used. The atom equivalents are determined through least-squares fitting of Eq. 3 to experimental heats of formation and quantum mechanical energies for several representative molecules. The atom equivalents correct for the error inherent in the calculation and in some cases, for the temperature and zero-point energy. Atom equivalent schemes are popular alternative methods for predicting heats of formation since they do not require high-level treatment of electron correlation or experimental input once the atom equivalents have been determined [16–20]. This approach was recently applied to small hydrocarbons [16] and a variety of organic compounds [20] using DFT. The Mole et al. study found that B3LYP/6-31G* predictions of heats of formation of 23 hydrocarbons had a root mean square (rms) deviation of 1.72 kcal/mol, with the maximum difference between experiment and prediction being 6.2 kcal/mol [16]. Heats of formation calculated using the 6-311+G** basis set improved the accuracy of the predictions to a rms deviation from experiment of 1 kcal/mol, and a maximum deviation of 2.34 kcal/mol. Habibollahzadeh et al. [20] used a similar procedure to predict the gas-phase heats of formation of 54 organic compounds using the Becke exchange and Perdew correlation functionals [21, 22] and the 6-31G(d,p) basis set [14]. The results have an average deviation from experiment of 3 kcal/mol.

We will follow the approach given in Ref. 16

to determine atom equivalents of carbon, nitrogen, hydrogen, and oxygen, the atomic species in most energetic materials. To do this, we first calculate a set of energies that correspond to optimized structures of energetic molecules for which heats of formation have been measured. We then determine the atom equivalents through least-squares fitting of Eq. 3 using the set of quantum mechanical energies and measured heats of formation. The ideal approach is to determine atom equivalents that do not depend on bond order or group component. However, there are several energetic molecules distinguished by different functional groups and different bond orders, but that have the same molecular formula. Because of this, we have determined the atom equivalents for atoms involved in a single Lewis structure (two-electron bond) or a multiple Lewis structure (greater than a two-electron bond, such as seen in aromatic groups and nitro groups). The heat of formation as given in Eq. 3 is therefore determined through seven atom equivalents, four representing atoms involved in single bonds (denoted as C, H, N, and O), and three representing atoms in multiple bonds (denoted as C', N', O'). The atom equivalents were determined by least-squares fitting of experimental heats of formation and B3LYP/6-31G* molecular energies for 35 molecules to Eq. 3.

Although Eq. 3 has been shown to be very accurate in the prediction of gas-phase heats of formation, often the standard state of the material of interest corresponds to the condensed phase. Thus, it is important to be able to predict the condensed-phase heats of formation. Condensed-phase heats of formation can be determined using the gas-phase heat of formation and heat of phase transition (either sublimation or vaporization) according to Hess' law of constant heat summation [11]:

$$\Delta H(\text{Solid}) = \Delta H(\text{Gas})$$

$$- \Delta H(\text{Sublimation}) \qquad (4)$$

$$\Delta H(\text{Liquid}) = \Delta H(\text{Gas})$$

$$- \Delta H(\text{Vaporization}). \qquad (5)$$

To evaluate Eqs. 4 and 5 using theoretical predictions alone, tools must be developed to predict enthalpies of phase change. Such tools have been developed by Politzer and coworkers for different types of organic compounds with a significant degree of success [23–29].

In a series of studies that investigate the relation of bulk properties of a material with molecular properties [23–29], Politzer and coworkers have clearly established that correlations exist between the electrostatic potential of a molecule and its condensed-phase properties, including the heats of sublimation [27] and vaporization [24, 26]. Functional relationships based on such correlations can be determined through the following procedure: First, Politzer et al. recommend determining the low-energy structure of a molecule through quantum mechanical prediction, then calculating the molecular surface area (SA) for this structure [23–29]. In this approach, the SA is defined to be that corresponding to the 0.001 electrons/bohr^3 isosurface of the electron density. Next, the electrostatic potential for this isosurface is used to generate two statistically based quantities, σ_{Tot}^2 and ν. σ_{Tot}^2 is described as an indicator of the variability of the electrostatic potential on the molecular surface, and ν is interpreted as showing the degree of balance between the positive and negative potentials on the molecular surface. From these quantities, the heat of vaporization can be represented as [24, 26]:

$$\Delta H(\text{Vaporization}) = a\sqrt{(\text{SA})} + b\sqrt{\sigma_{Tot}^2\nu} + c$$

$$(6)$$

where a, b, and c are fitting parameters. Similarly, the heat of sublimation can be represented as [27]:

$$\Delta H(\text{Sublimation}) = a(\text{SA})^2 + b\sqrt{\sigma_{Tot}^2\nu} + c$$

$$(7)$$

The parameters a, b, and c in Eqs. 6 and 7 are determined from least-squares fitting to reliable values of the enthalpies of phase change. Politzer et al. applied this procedure to develop a predictive tool for the heats of sublimation of 34 organic compounds [27]. The predictions using the tool had a standard deviation of 2.5 kcal/mol from experimental values. Politzer et al. also used this tool with one developed to calculate gas-phase heats of formation to pre-

dict solid-phase heats of formation for five compounds [27]. In this application, the average deviation from experiment was 2.8 kcal/mol. In a similar application, Politzer and Murray predicted heats of vaporization using Eq. 5 for 41 compounds that have a standard deviation of 0.6 kcal/mol [26].

We have followed the Politzer et al. approach to develop tools to predict the heats of sublimation and vaporization of energetic materials, then combined these with Eq. 3 to predict solid and liquid heats of formation. The only significant difference in the work presented here and that presented by Politzer and coworkers is the level of theory and the set of molecules used in parameterizing Eqs. 6 and 7.

COMPUTATIONAL DETAILS

Generalized gradient approximation (GGA) DFT [4–7] geometry optimizations of all species reported herein were performed using the 6-31G* basis set [14] and the hybrid B3LYP [9, 10] density functional. This modest level of theory was chosen due to the size of some of the molecules used in the study. The 6-31G* basis set has been shown to be reasonably accurate when used with the B3LYP density functional [16, 30]. The B3LYP density functional has been shown to reproduce experimental properties and is commonly thought to be one of the most reliable of the available density functionals [1, 8, 31]. The calculations were performed using the Gaussian 94 (G94) suite of quantum chemistry programs [32]. All calculations were subject to the default settings of G94.

The atom equivalents in Eq. 3 are determined by fitting to experimental gas-phase heats of formation and corresponding quantum mechanical energies of optimized structures of several energetic molecules. The quantum mechanical energies of the molecules whose names are followed by a "g" in Table 1 were used in the fitting of Eq. 3. Many of the molecules used in the fitting are large polyatomic molecules, and most likely have several different stable conformations that are similar in energy. We did not perform a search in conformation space for each of these molecules to determine the molecular structure associated with the global min-

imum, but have assumed that the energy of the local minima are within a few kcal/mol of the global minimum. Eqs. 6 and 7 are also parameterized through least-squares fitting to experimental data and information from the quantum-mechanically-derived electrostatic potential of individual molecules, as described previously. Equations 6 and 7 were fitted using 27 and 36 sets of experimental data for heats of vaporization and sublimation, respectively. The molecules used in parameterizing Eqs. 6 and 7 are also given in Table 1. Their names are followed by a "v" or "s" to denote that they were used for parameterizing the equations for the heat of vaporization or sublimation, respectively.

RESULTS AND DISCUSSION

Atom equivalents obtained through least-squares fitting of Eq. 3 are given in Table 2. A comparison of the experimental and the predicted gas-phase heats of formation using Eq. 3 is given in Table 3. A visual comparison of the predictions with experiment is provided in Fig. 1. The rms deviation of the predictions from experiment is 3.1 kcal/mol. The maximum deviation of the predictions from the experimental values is 7.3 kcal/mol for azidomethylbenzene. The next largest difference occurs for cyanogen azide (6.2 kcal/mol). This is not surprising, since only two azido- compounds were used in the fitting.

The best-fit parameters for Eqs. 6 and 7 are given in Table 2, and the predicted heats of vaporization and sublimation are given in Table 3 for comparison with the experimental information used in the fitting. Figures 2 and 3 show the results of the fits for the heats of vaporization and sublimation, respectively. The rms deviation of the predictions from the experimental heats of vaporization is 1.7 kcal/mol. The maximum deviation from experiment is 6.1 kcal/mol for nitroglycerin, with the next largest difference being 2.9 kcal/mol for trinitromethane. The rms deviation of the predictions from experimental heats of sublimation is 3.6 kcal/mol, with the maximum deviation being 12.4 kcal/mol for hexanitroethane. The next largest difference between experiment and prediction is 5.3 kcal/mol for dinitromethylbenzene.

TABLE 1

B3LYP/6-31G* Molecular Properties Used in Eqs. 3, 6, and 7

Name	Expt.[a]	C	H	N	O	C'	N'	O'	Absolute Energy (hartrees)	SA (Å²)	ν	σ^2_{Tot} (kcal/mol)²
Cyanogen azide	g	0	0	0	0	1	4	0	−257.002988577	97.646679	0.249860	207.859558
Tetranitromethane	g, v	1	0	0	0	0	4	8	−858.413321934	166.035026	0.052589	82.899727
Trinitromethane	v, s	1	1	0	0	0	3	6	−653.956381558	144.477765	0.043476	259.188354
Hexanitroethane	g, s	2	0	0	0	0	6	12	−1306.656763240	212.868693	0.064430	119.363091
Dinitromethane	g, v	1	2	0	0	0	2	4	−449.487256631	118.551923	0.100087	240.648117
Methyl nitrite	g, v	1	3	0	1	0	1	1	−245.007962059	89.882874	0.249936	56.139923
Nitromethane	g, v	1	3	0	0	0	1	2	−245.009330800	89.818926	0.246111	108.135544
Methyl nitrate	g, v	1	3	0	1	0	1	2	−320.189434600	100.572911	0.249294	79.381935
Nitroguanidine		0	4	2	0	1	2	2	−409.855059996	124.063733	0.230870	435.239868
Nitroethane	v	2	5	0	0	0	1	2	−284.328086959	110.468975	0.229348	103.713966
Ethyl nitrite		2	5	0	1	0	1	1	−284.325006418	115.069420	0.213790	60.119099
Ethyl nitrate	g, v	2	5	0	1	0	1	2	−359.508395169	121.367742	0.241344	69.094345
Dimethylnitramine	g, s	2	6	1	0	0	1	2	−339.656549984	123.494464	0.200675	140.171310
Nitroglycerin	g, v	3	5	0	3	0	3	6	−958.168013834	218.847052	0.111295	132.965546
TTT (Hexahydro-1,3,5-trinitroso-1,3,5-triazine)	g, s	3	6	3	0	0	3	3	−671.860924393	181.137911	0.211136	162.981583
RDX (Hexahydro-1,3,5-trinitrotriazine)	g, s	3	6	3	0	0	3	6	−897.408901632	201.594799	0.149852	196.611298
1-Nitropropane	v	3	7	0	0	0	1	2	−323.641585437	132.373802	0.199392	92.913933
2-Nitropropane	v	3	7	0	0	0	1	2	−323.645738999	129.743605	0.182169	91.661804
Propyl nitrite	g, v	3	7	0	1	0	1	1	−323.638914025	136.474131	0.181451	56.687702
n-Propyl nitrate	v	3	7	0	1	0	1	2	−398.820582169	140.472688	0.238864	70.809593
3,4-Furazandimethanol dinitrate	g, v	2	4	0	3	2	4	4	−900.030164899	211.827748	0.127652	123.151146
1,4-Dinitrosopiperazine	g, s	4	8	2	0	0	2	2	−526.543460553	168.541711	0.225159	111.991249
1,4-Dinitropiperazine	g, s	4	8	2	0	0	2	4	−676.910151215	184.191543	0.249480	110.465118
HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)		4	8	4	0	0	4	8	−1196.545948910	245.151259	0.188715	196.189636
2-Methyl-2-nitropropane	g	4	9	0	0	0	1	2	−362.961528577	144.467749	0.159268	97.889603
1-Nitrobutane	v	4	9	0	0	0	1	2	−362.954119935	151.853360	0.180655	91.500481
2-Nitrobutane	v	4	9	0	0	0	1	2	−362.958529381	148.815487	0.145739	86.887459
t-Butyl nitrite	g, v	4	9	0	1	0	1	1	−362.958313184	149.240879	0.161770	66.320312
n-Butyl nitrite	g, v	4	9	0	1	0	1	1	−362.952557150	157.775266	0.178047	57.120720
PETN (Tetranitrate pentaerythritol)	s	5	8	0	4	0	4	8	−1316.468455720	291.516975	0.104211	116.481842
1-Nitropiperidine	g	5	10	1	0	0	1	2	−456.398610158	163.824522	0.095410	123.016701
1,3,5-Trinitrobenzene	s	0	3	0	0	6	3	6	−845.736696893	202.532990	0.188445	108.958405
2,4,6-Trinitrophenol		0	3	0	1	6	3	6	−920.954678338	207.730401	0.198037	135.451736
2,4,6-Trinitroresorcinol		0	3	0	2	6	3	6	−996.177452790	214.610239	0.194153	150.847977
1-Nitro-2-nitrosobenzene	s	0	4	0	0	6	2	3	−565.992564774	164.664846	0.249159	103.950478
1-Nitro-3-nitrosobenzene	s	0	4	0	0	6	2	3	−566.036632071	168.137290	0.249814	99.408859
1,2-Dinitrobenzene		0	4	0	0	6	2	4	−641.229491455	175.485624	0.247027	125.204185
1,3-Dinitrobenzene	s	0	4	0	0	6	2	4	−641.246252172	176.131173	0.248380	97.582031
1,4-Dinitrobenzene		0	4	0	0	6	2	4	−641.246008400	175.928160	0.249999	84.098793
2,4-Dinitrophenol		0	4	0	1	6	2	4	−716.473897710	182.360129	0.249977	103.774368
2,6-Dinitrophenol		0	4	0	1	6	2	4	−716.461450000	180.503403	0.246903	124.667587
2,4,6-Trinitroaniline		0	4	1	0	6	3	6	−901.105946802	209.342650	0.218842	125.144867
Nitrosobenzene	g	0	5	0	0	6	1	1	−361.539779255	142.410932	0.199211	146.791779
Nitrobenzene	g, v	0	5	0	0	6	1	2	−436.750579273	150.299993	0.215926	154.002136
2-Nitrophenol	g, s	0	5	0	1	6	1	2	−511.976038167	156.500748	0.236806	114.630844
3-Nitrophenol	g, s	0	5	0	1	6	1	2	−511.966822213	159.153839	0.232478	248.392502
4-Nitrophenol	g, s	0	5	0	1	6	1	2	−511.969008406	159.159240	0.234619	305.803284
m-Nitroaniline	g, s	0	6	1	0	6	1	2	−492.104971819	164.287003	0.248321	256.141357

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TABLE 1

(Continued)

Name	Expt.[a]	C	H	N	O	C'	N'	O'	Absolute Energy (hartrees)	SA (Å²)	ν	σ^2_{Tot} (kcal/mol)²
o-Nitroaniline	s	0	6	1	0	6	1	2	−492.109521689	160.796544	0.247430	232.851974
TATB (2,4,6-trinitro-1,3,5-benzenetriamine)		0	6	3	0	6	3	6	−1011.833118600	221.751885	0.249990	116.236404
DNPN [N-Nitrobis-(2,2-dinitropropyl)amine]	g	6	10	1	0	0	5	10	−1314.872258970	276.518965	0.206557	141.827118
TNT (trinitrotoluene)	g,s	1	5	0	0	6	3	6	−885.045499312	217.011451	0.215058	94.741478
2-Methoxy-1,3,5-trinitrobenzene	s	1	5	0	1	6	3	6	−960.240793345	226.444172	0.221238	96.778053
Tetryl (N-methyl-N,2,4,6-tetranitroaniline)		1	5	1	0	6	4	8	−1144.856680870	251.412792	0.178351	141.468536
1-Methyl-2,4-dinitrobenzene	g,s	1	6	0	0	6	2	4	−680.561775882	192.841213	0.246866	90.642029
2-Methyl-1,3-dinitrobenzene		1	6	0	0	6	2	4	−680.553580234	190.525356	0.248539	98.388885
Dinitromethylbenzene	g,s	1	6	0	0	6	2	4	−680.543248757	196.337841	0.237477	122.123009
2-Methyl-4,6-dinitrophenol		1	6	0	1	6	2	4	−755.792238817	201.448137	0.236338	91.450188
Azidomethylbenzene	g,v	1	7	0	0	6	3	0	−435.144931168	179.499171	0.232174	65.953873
Nitromethylbenzene	g,v	1	7	0	0	6	1	2	−476.061676752	172.640031	0.199769	129.356613
1-Methyl-4-nitrobenzene	g,s	1	7	0	0	6	1	2	−476.069640689	171.147817	0.171034	158.963928
2,4,6-Trinitrometaxylene		2	7	0	0	6	3	6	−924.357319040	232.435743	0.244814	73.367279
1,3-Dimethyl-2-nitrobenzene	g,v	2	9	0	0	6	1	2	−515.379313077	185.404942	0.162293	130.591660
1,3,5-Trimethyl-2,4,6-trinitrobenzene		3	9	0	0	6	3	6	−963.668410824	248.796721	0.248856	57.152065
1-Nitronaphthalene	s	0	7	0	0	10	1	2	−590.387677028	194.108673	0.198561	159.976227
2,2',4,4',6,6'-Hexanitrostilbene	g	0	6	0	0	14	6	12	−1767.644192350	381.660470	0.166741	119.739990
ε-Hexaazaisowurtzitane		6	6	6	0	0	6	12	−1791.180675600	312.693403	0.065415	230.603210
β-Hexaazaisowurtzitane		6	6	6	0	0	6	12	−1791.183184600	314.537686	0.071639	213.575226
Dinitrate diethylene glycol		4	8	0	3	0	2	4	−793.010912406	218.336681	0.243205	69.461563

[a] Symbols denote experimental values are available for gas-phase heats of formation (g), heats of vaporization (v), and heats of sublimation (s) and are used in parameterizing Eqs. 3, 6, and 7.

Table 3 also contains comparisons of predictions and experimental values for liquid and solid heats of formation. There are 41 experimental values of liquid heats of formation that

correspond to 24 molecules. These are compared with predictions using Eqs. 3 and 6. Figure 4 provides a visual comparison of the predictions and experiment. The rms deviation

TABLE 2

Atom Equivalents and Parameters for Eqs. 6 and 7

Equation 3					
Atom Equivalents	ϵ (hartrees)	Equation 6		Equation 7	
C	−38.121621	a (kcal/mol-Å^{-1})	1.818689	a (kcal/mol-Å^{-4})	4.234303×10^{-4}
H	−0.592039	b (kcal/mol)	1.3321583	b (kcal/mol)	2.5793785
N	−54.774096	c (kcal/mol)	−16.142460	c (kcal/mol)	−6.7335407
O	−75.161771				
C'	−38.121380				
N'	−54.765886				
O'	−75.157348				

TABLE 3

Heats of Formation, Heat of Vaporization, and Heat of Sublimation (kcal/mol)[a]

Name	ΔH_f° Gas			Liquid			Solid			ΔH_{vap}°			ΔH_{sub}°		
	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.
Cyanogen azide	108. ± 5.	114.2	6.2												
Tetranitromethane	19.7 ± 0.5	19.2	−0.5	9.2 ± 0.4	9.1	−0.1				11.94	10.1	−1.8			
				8.8 ± 0.7		0.3				10.5 ± 0.1		−0.4			
				9.85 ± 1.00		−0.8									
Trinitromethane				−16.25 ± 0.75	−10.8	5.5	−11.5 ± 0.5	−11.4	0.1	13.1	10.2	−2.9	11.2 ± 0.1	10.8	−0.4
				−7.68		−3.1							11.0 ± 0.10		−0.2
				−18.63		7.8									
Hexanitroethane	42.8 ± 1.4	43.9	1.1				25.9 ± 1.0	24.3	−1.6				16.9 ± 0.4	19.6	2.7
							28.6 ± 1.9		−4.3				7.2		12.4
Dinitromethane	−14.07 ± 1.02	−12.8	1.3	−25.07 ± 0.20	−23.0	2.1				11.0	10.2	−0.8			
Methyl nitrite	−15.64 ± 0.20	−15.8	−0.2	−16.05 ± 0.20	−21.9	−5.9				5.40 ± 0.04	6.1	0.7			
	−16.8 ± 0.8		1.0	−20.33 ± 0.25		−1.6									
	−14.93 ± 0.26		−0.9												
Nitromethane	−19.3 ± 0.3	−19.5	−0.2	−26.9 ± 0.1	−27.4	−0.5				9.168	8.0	−1.2			
				−27.3 ± 0.15		−0.4				9.171		−1.2			
				−21.28 ± 0.18		−6.1				9.09 ± 0.09		−1.1			
										8.24 ± 0.02		−0.2			
Methyl nitrate	−29.2 ± 0.3	−31.0	−1.8							8.150	8.0	−0.2			
Nitroguanidine							−20.7 ± 0.59	−7.4	13.3						
							−23.4 ± 1.0		16.0						
							−21.3		13.9						
Nitroethane				−34.4 ± 0.1	−37.1	−2.7				9.94 ± 0.10	9.5	−0.4			
				−34.32 ± 0.26		−2.8									
				−33.48 ± 0.31		−3.6									
Ethyl nitrite	−25.9[b]	−22.9	3.0												
Ethyl nitrate	−37.0 ± 0.8	−39.3	−2.3	−45.51 ± 0.25	−48.6	−3.1				8.670	9.3	0.6			
				−45.7 ± 0.8		−2.9				8.7		0.6			
Dimethylnitramine	−1.2 ± 0.3	−4.0	−2.8	−17.0 ± 1.0	−15.1	1.9	−17.9 ± 0.3	−17.4	0.5						
Nitroglycerin	−66.71 ± 0.65	−72.7	−6.0	−88.4 ± 0.5	−88.6	−0.2				22.0 ± 0.50	15.9	−6.1	9.89 ± 0.50	13.4	3.5
				−88.70 ± 0.41		0.1							16.70		−3.3
				−89.6		1.0									
				−89.0 ± 0.9		0.4									
				−84.58		−4.0									

TABLE 3

Heats of Formation, Heat of Vaporization, and Heat of Sublimation (kcal/mol)^a

Name	ΔH_f° Gas			ΔH_f° Liquid			ΔH_f° Solid			ΔH_{vap}°			ΔH_{sub}°		
	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.
TTT (Hexahydro-1,3,5-trinitroso-1,3,5-triazine)	94.3	93.0	−1.3				68.3	70.7	2.4				26.9	22.3	−4.6
							68.32 ± 0.56		2.4						
RDX (Hexahydro-1,3,5-trinitrotriazine)	45.8	45.3	−0.5				18.9 ± 1.2	20.8	1.9				26.79	24.5	−4.5
							14.7		6.1				26.8 ± 0.5		−2.3
							15.90 ± 0.50		4.9						
1-Nitropropane	−28.4 ± 1.0	−28.1	0.3	−40.0 ± 0.1	−43.1	−3.1				10.37 ± 0.10	10.5	0.1			
				−40.35 ± 0.30		−2.8									
				−40.05 ± 0.61		−3.1									
2-Nitropropane				−43.09 ± 0.20	−45.2	−2.1				9.88 ± 0.10	10.0	0.1			
				−43.78 ± 0.17		−1.4									
Propyl nitrite	2.6 ± 0.6	1.4	−1.2	−36.0	−37.5	−1.5				7.6	9.4	1.8			
n-Propyl nitrate				−51.27 ± 0.3	−54.3	−3.0				9.7	10.9	1.2			
3,4-Furazandimethanol dinitrate				−11.40 ± 0.40	−14.2	−2.8				14.00 ± 0.20	15.6	1.6			
1,4-Dinitrosopiperazine	46.4 ± 0.7	46.4	0.0				22.2 ± 0.5	28.2	6.0				24.2 ± 0.2	18.2	−6.0
1,4-Dinitropiperazine	13.9 ± 0.6	13.8	−0.1				−12.7 ± 0.4	−7.4	5.3				26.6 ± 0.2	21.2	−5.4
HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)							18.	25.6	7.6						
							24.5 ± 0.66		1.1						
2-Methyl-2-nitropropane	−42.32 ± 0.79	−41.5	0.8	−46.03 ± 0.32	−48.5	−2.5	−54.9 ± 0.6	−53.8	1.1						
1-Nitrobutane	−41.0 ± 1.0	−36.7	4.3	−49.61 ± 0.36	−50.4	−0.8				11.61 ± 0.12	11.7	0.1			
2-Nitrobutane	−34.8 ± 1.0	−33.1	1.7	−49.2	−47.1	2.1				10.48 ± 0.10	10.8	0.3			
t-Butyl nitrite				−43.6	−44.0	−0.4				8.2	10.4	2.2			
n-Butyl nitrite										8.8	11.0	2.2			
PETN (Tetranitrate pentaerythritol)							−128.7 ± 0.2	−135.3	−6.6				36.3 ± 0.5	38.2	1.9
1-Nitropiperidine	−10.6 ± 0.6	−9.7	0.9	−22.2 ± 0.4	−21.4	0.8									
1,3,5-Trinitrobenzene							−8.9 ± 0.3	−16.4	−7.5				23.8 ± 0.5	22.3	−1.5

TABLE 3

Heats of Formation, Heat of Vaporization, and Heat of Sublimation (kcal/mol)[a]

Name	ΔH_f Gas			ΔH_f Liquid			ΔH_f Solid			ΔH_{vap}			ΔH_{sub}°		
	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.
2,4,6-Trinitrophenol							-52.075 ± 0.476	-54.2	-2.1						
							-51.14 ± 0.32		-3.1						
							-53.76		-0.4						
2,4,6-Trinitroresorcinol							-111.74 ± 1.65	-94.4	17.3						
							-103.5		9.1						
							-129.76		35.4						
1-Nitro-2-nitrosobenzene							24.45	49.7	25.2				$13.$	17.9	4.9
1-Nitro-3-nitrosobenzene							25.08	21.8	-3.3				15.0	18.1	3.1
1,2-Dinitrobenzene							-0.4 ± 0.15	-3.0	-2.6						
1,3-Dinitrobenzene							-6.5 ± 0.1	-12.0	-5.5				19.4 ± 0.41	19.1	-0.3
							-4.59								
1,4-Dinitrobenzene							-9.2 ± 0.1	-10.9	-1.7						
2,4-Dinitrophenol							-56.29	-54.7	1.6						
							-53.31								
2,6-Dinitrophenol							-50.105 ± 0.782	-47.8	2.3						
2,4,6-Trinitroaniline							-17.4	-21.3	-3.9						
							-27.69		6.4						
Nitrosobenzene	48.1 ± 1.0	45.1	-3.0												
Nitrobenzene	16.38 ± 0.16	11.6	-4.8	2.98 ± 0.13	-2.2	-5.2				13.148 ± 0.0043	13.8	0.7			
2-Nitrophenol	-31.62 ± 0.33	-28.4	3.2				-48.90 ± 0.33	-45.4	3.5				17.28 ± 0.067	17.1	-0.2
	-30.78 ± 0.38		2.4				-48.37 ± 0.24		3.0						
							-47.64		2.2						
3-Nitrophenol	-26.12 ± 0.26	-22.6	3.5				-47.92 ± 0.24	-46.2	1.7				21.80 ± 0.12	23.6	1.8
	-25.22 ± 0.43		2.6				-49.16 ± 0.41		3.0				23.95 ± 0.1		-0.4
													23.95 ± 0.1		-0.4
4-Nitrophenol	-27.41 ± 0.29						-49.50 ± 0.26	-49.8	-0.3				22.08 ± 0.10	25.8	3.7
	-28.13 ± 0.48						-50.76 ± 0.24		1.0						
							-54.19		4.4						
m-Nitroaniline	14.9 ± 0.43	19.0	4.1				-8.17 ± 0.29	-6.3	1.9				23.1 ± 0.07	25.3	2.2
							-9.2 ± 0.1		2.9				23.1 ± 0.3		2.2
							-6.76		0.5						
							-15.17		8.9						

TABLE 3

Heats of Formation, Heat of Vaporization, and Heat of Sublimation (kcal/mol)^a

Name	ΔH°_f Gas			ΔH°_f Liquid			ΔH°_f Solid			ΔH°_{vap}			ΔH°_{sub}		
	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.
o-Nitroaniline							−6.3 ± 0.1	−7.7	−1.4				22. ± 0.72	23.8	1.8
							−6.29		−1.4				22. ± 1.0		1.8
TATB (2,4,6-trinitro-1,3,5-benzenetriamine)							−17.854 ± 0.708	−20.8	−2.9						
							−33.4 ± 1.2		12.6						
							−36.9		16.1						
DNPN [N-Nitrobis-(2,2-dinitropropyl)amine]	−31.7 ± 0.6	−28.3	3.4				−55.4	−67.9	−12.5						
TNT (Trinitrotoluene)	5.75 ± 0.84	4.0	−1.8				−15.1 ± 1.2	−20.9	−5.8				25.00 ± 0.41	24.8	−0.2
							−19.25 ± 0.74		−1.7				25.0 ± 0.4		−0.2
													28.3		−3.5
2-Methoxy-1,3,5-trinitrobenzene							−11.94		−9.0				31.81 ± 0.50	26.9	−4.9
							−44.75	−44.0	0.8						
Tetryl (N-methyl-N,2,4,6-tetranitroaniline)							9.8 ± 1.1	−1.7	−11.5						
							7.34		−9.0						
1-Methyl-2,4-dinitrobenzene	7.93 ± 0.79	1.0	−6.9				−15.87 ± 0.72	−20.3	−4.4				23.8 ± 0.3	21.2	−2.6
							−9.5		−10.8				23.8 ± 0.31		−2.6
													23.8 ± 0.60		−2.6
2-Methyl-1,3-dinitrobenzene							−13.199 ± 0.5368	−15.3	−2.1						
							−9.99		−5.3						
Dinitromethyl benzene	8.3 ± 1.6	12.6	4.3				−9.9 ± 1.4	−10.9	−1.0				18.2 ± 0.2	23.5	5.3
2-Methyl-4,6-dinitrophenol							−66.7	−64.6	2.1						
Azidomethylbenzene	99.5 ± 0.4	92.2	−7.3	88.0 ± 0.3	78.7	−9.3				11.5 ± 0.1	13.4	1.9			
Nitromethylbenzene	7.34 ± 0.68	8.2	0.9	−5.46 ± 0.61	−6.3	−0.8				12.8 ± 0.3	14.5	1.7			

TABLE 3

Heats of Formation, Heat of Vaporization, and Heat of Sublimation (kcal/mol)[a]

Name	ΔH°_f Gas			ΔH°_f Liquid			ΔH°_f Solid			ΔH°_{vap}			ΔH°_{sub}		
	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.	Expt.	Theo.	Diff.
1-Methyl-4-nitrobenzene	7.38 ± 0.94	3.2	−4.2				−11.52 ± 0.72	−15.9	−4.4				18.9 ± 0.60	19.1	0.2
2,4,6-Trinitrometaxylene							−19.87	−26.9	−7.0				18.9 ± 0.6		0.2
1,3-Dimethyl-2-nitrobenzene	2.1 ± 0.38	0.7	−1.4	−12.1 ± 0.31	−14.0	−1.9				14.2 ± 0.2	14.8	0.6			
1,3,5-Trimethyl-2,4,6-trinitrobenzene							−29.75	−32.4	−2.7						
1-Nitronaphthalene							10.93	8.2	−2.7				25.60 ± 0.50	23.8	−1.8
2,2′,4,4′,6,6′-Hexanitrostilbene	56.98	57.0	0.02				16.2 ± 2.5	−9.5	−25.7						
							13.88		−23.4						
ε-Hexaazaisowurtzitane							90.2 ± 3.11[c]	99.2	9.0						
β-Hexaazaisowurtzitane							103.01 ± 3.11[c]	97.1	−5.9						
Dinitrate diethylene glycol				−107.8	−105.1	2.7	−113.8	−112.9	0.9						

[a] Ref. 33

[b] Uses unconventional sign.

[c] Ref. 34.
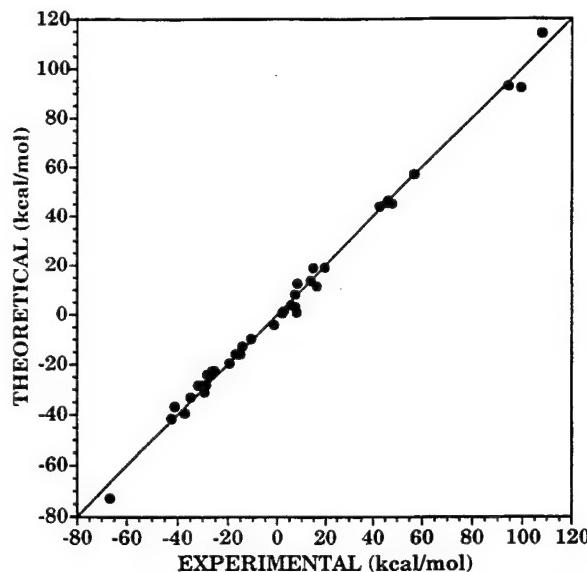
Fig. 1. Calculated gas-phase heats of formation versus experimental values for 35 energetic molecules. The solid line represents exact agreement between the predictions and experiment.

Fig. 3. Same as Fig. 1, except for heats of sublimation. Comparisons are made using 36 experimental values.

of the predicted liquid heats of formation from experiment is 3.3 kcal/mol, and the maximum deviation from experiment is 9.3 kcal/mol for azidomethylbenzene, followed by one of the values reported for trinitromethane. Note that three values are reported for trinitromethane; these range from -7.68 to -18.63 kcal/mol. The predicted value is -10.8 kcal/mol. The only molecular species in Fig. 4 for which no experimental information was used in parameterizing Eqs. 3 or 6 is dinitrate diethylene glycol; the predicted liquid heat of formation is within 3 kcal/mol of the experimental result.

Seventy-five experimental values for solid heats of formation corresponding to 44 molecules are given in Table 3 for comparison with predictions using Eqs. 3 and 7. Figure 5 provides a visual comparison between experiment and the predictions. The rms deviation of the predictions from experiment is 9.0 kcal/mol, and the maximum deviation of 35.4 kcal/mol corresponds to one of the reported values for trinitroresorcinol. As evident from Table 3, there

Fig. 2. Same as Fig. 1, except for heats of vaporization. Comparisons are made using 27 experimental values.
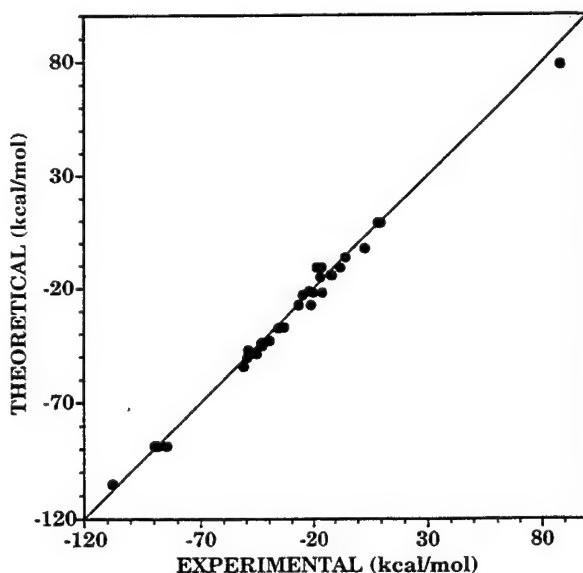
Fig. 4. Same as Fig. 1, except for liquid-phase heats of formation. Comparisons are made using 41 experimental values.
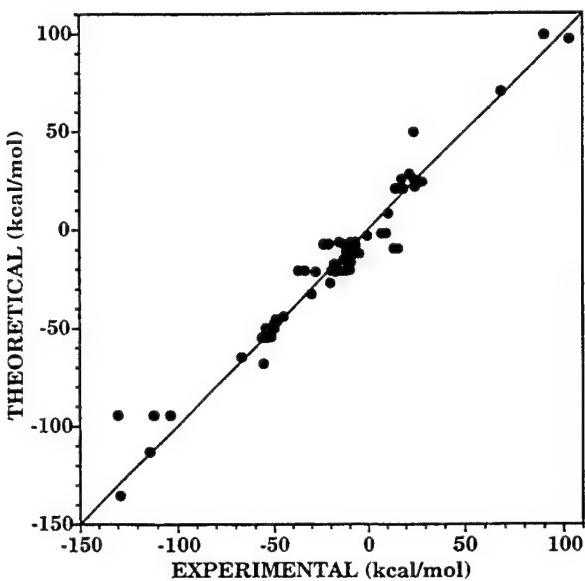
Fig. 5. Same as Fig. 1, except for solid-phase heats of formation. Comparisons are made using 75 experimental values.


Fig. 6. Same as Fig. 5, except it shows a comparison between predictions and experiment for 18 molecular species from which no information was used in developing the predictive tools described in this work.

are several species for which notably different values are reported for the heat of formation. The values reported for solid heats of formation for trinitroresorcinol, for example, range from -103.5 to -129.8 kcal/mol. The predicted heat of formation deviates from one of the reported values by 35.4 kcal/mol, which is the maximum deviation of all of the predictions. The same prediction, however, is within 9 kcal/mol of one of the other reported values for trinitroresorcinol. The next largest deviation of the predictions from experiment is for hexanitrostilbene, which is ~26 kcal/mol.

Eighteen of these molecular species were not used in the parameterization of Eqs. 3 or 7, and thus the results for these can be considered as completely predicted, rather than reflecting the degree of the goodness of the fitting of Eqs. 3 and 7. Figure 6 shows the comparison of the predictions from experiment. The rms deviation of the predictions from experiment for these 18 molecular species is 10.3 kcal/mol, respectively, and the maximum deviation from experiment is 11.5 kcal/mol for Tetryl. Four of the 18 species have multiple values reported for heats of formation that differ from one another by more than 5 kcal/mol. The values reported for HMX differ by 6.5 kcal/mol; those of 2,4,6-trinitroresorcinol differ by 26.3 kcal/mol; those of 2,4,6 trinitroaniline differ by 10.3 kcal/mol; and those

of TATB differ by 19.1 kcal/mol. Such disparities in experimental measurement contribute to the collective rms deviation of the predictions from experiment.

CONCLUSIONS

A series of computational tools have been developed that use only quantum mechanical information to predict gas- and condensed-phase heats of formation, heats of vaporization, and heats of sublimation. Quantum mechanical energies of molecules are converted to gas-phase heats of formation using the method of atom equivalents [16]. The predictions for 35 molecules have a rms deviation from experimental results of 3.1 kcal/mol. Surface electrostatic potentials of individual molecules were generated and used in empirical equations for heats of sublimation and vaporization as recommended by Politzer and coworkers [23–29]. These functions were parameterized using 27 and 36 sets of experimental values for the heats of vaporization and sublimation, respectively. The rms deviation of the heats of vaporization calculated using this function is 1.7 kcal/mol. The rms deviation of heats of sublimation from experimental values is 3.6 kcal/mol. The equa-

tions for heats of vaporization and sublimation are used with the atom-equivalent method for calculating the gas-phase heats of formation to predict liquid and solid heats of formation. The liquid heats of formation have a rms deviation from 41 experimental values of 3.3 kcal/mol. The rms deviation of the solid heats of formation from 75 experimental values is 9.0 kcal/mol.

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Quantum mechanical calculations are used to predict gas, liquid, and solid heats of formation of energetic molecules. A simple atom-equivalent method converts quantum mechanical energies of molecules and their atomic constituents to gas-phase heats of formation of energetic materials. Functional relationships between heats of vaporization and sublimation and properties associated with quantum, mechanically determined electrostatic potentials of isolated molecules are established. These are used with the gas-phase heats of formation to predict condensed-phase heats of formation. The calculated gas-phase heats of formation have a root mean square (rms) deviation of 3.1 kcal/mol and a maximum deviation of 7.3 kcal/mol from 35 experimental values. The rms and maximum deviation of predicted heats of vaporization from 27 experimental values are 1.7 and 6.1 kcal/mol, respectively. The rms and maximum deviations of predicted heats of sublimation from 36 experimental values are 3.6 and 12.4 kcal/mol, respectively. The rms and maximum deviations of predictions of liquid heats of formation from 41 measured values (corresponding to 24 molecules) are 3.3 and 9.3 kcal/mol, respectively. Similarly, the rms and maximum deviations of predictions of solid heats of formation from 75 measured values (corresponding to 44 molecules) are 9.0 and 35.4 kcal/mol, respectively.

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